

Condensed Matter

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Structural properties of $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ ($x \leq 1$) solid solution thin film obtained by EXAFS

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For the solid solution system $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ XRD measurements revealed an increase of the cell volume as a function of alloying parameter x , but did not provide selective information about the geometric structure. Therefore, EXAFS measurements were performed on thin films of $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ at the K shells of the metal ions In, Cu and Zn. Three bond lengths corresponding to the nearest neighbour metal-sulfur distances were identified. These bond lengths remain nearly constant over the whole composition range of the solid solution system. This phenomenon, already known for binary compounds, is now observed for the first time a ternary system as well.

The information gained by EXAFS was combined with electronic structure calculations to understand the highly nonlinear dependence of the band gap on x observed in the composition range $0 \leq x \leq 0.25$.

Keywords: EXAFS; solid solution system; chalcopyrite.

1. Introduction

Solid solution systems have been subject of investigation for a long time, because of the possibility to tailor material properties. For many alloys the lattice constant, measured by x-ray diffraction (XRD), varies linearly with the composition (Mikkelsen & Boyce 1983). Accordingly, one of the most commonly used models to describe solid solutions is the virtual-crystal approximation (VCA), which assumes average atomic positions, bond lengths, bond ionicities, etc. In contrast, Extended X-ray fine structure (EXAFS) spectroscopy is well suited to study the near neighbour spacing of a specific atom in solid solution systems. For example, in $\text{Ga}_{1-x}\text{In}_x\text{As}$ was found, that the Ga-As and In-As nearest neighbour distances remain nearly constant over the whole composition range (Mikkelsen & Boyce 1983). Similar results were also observed for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ (Miyano et al. 1997).

The solid solution system $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ attracts interest due to its optoelectronic properties. Recent experiments show a highly nonlinear dependence of optical band-gap upon the alloying parameter x (Luck et al. 1996). Furthermore, this solid solution shows a phase transition from cubic to tetragonal at $x = 0.81 \pm 0.02$, coupled with a discontinuous change of lattice

constants and mole volume (Bente & Doering 1991). In the cubic and tetragonal range of this solid solution system, the lattice constants and the mole volumina are linearly dependent upon the composition x . In order to shed some light on the influence of electronic and geometric structure on the band gap, band structure calculations were performed for several compositions of $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ (Eyert et al. 1997; Luck 1997). The calculated variation of the optical band gap is in almost quantitative agreement with experimental data.

Here we report on EXAFS measurements on $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ thin films to study the local atomic distances.

2. Experimental

The experiments were performed at the E4 and RÖMO II stations at HASYLAB. EXAFS spectra were taken at the Cu, Zn and In K-edges. The measurements were carried out at room temperature and at $T = 20$ K (see Fig. 1). For CuInS_2 measurements in the transmission mode were possible. Several samples with different x from the $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ solid solution system were prepared as thin, polycrystalline films on soda lime glass substrates in a high vacuum chamber by the coevaporation of Cu, In, S and ZnS. The film thickness was roughly $3 \mu\text{m}$. Thus only measurements in fluorescence mode were possible.

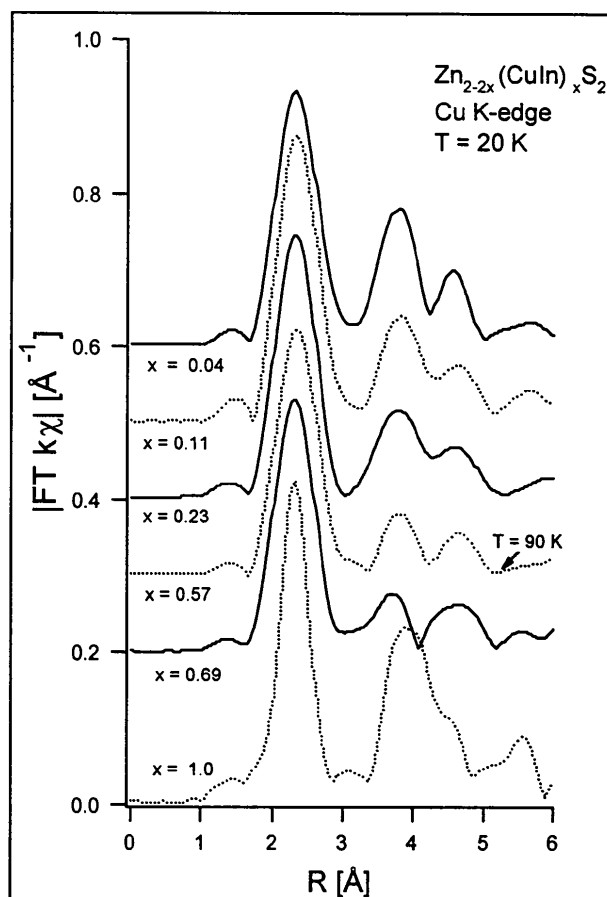


Figure 1

The Fourier transforms of the EXAFS oscillation of $\text{Zn}_{2-2x}(\text{CuIn})_x\text{S}_2$ with different x measured at Cu K-edges.

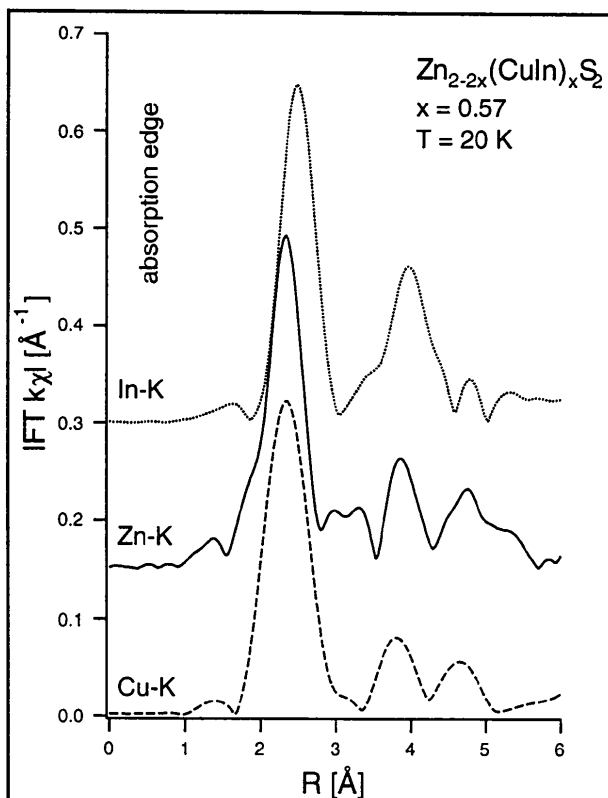


Figure 2

The Fourier transforms of the EXAFS oscillation of $Zn_{2-2x}(CuIn)_xS_2$ with $x = 0.57$ measured at different absorption edges.

The EXAFS analysis was performed using FEFF 7.02 (Ankudinov & Rehr 1997) and FEFFIT 3.42 codes (Newville et al. 1995). The structural parameters such as the atomic distances R_i and the Debye-Waller parameters σ_i with $i = 1, 2, 3$ were extracted. For the Fourier transformed (FT) k weighted EXAFS oscillation (typical k range $2.5-16 \text{ \AA}^{-1}$) a Gaussian window was used.

3. The solid solution system $Zn_{2-2x}(CuIn)_xS_2$

Fig. 1 shows the FT of the $Zn_{2-2x}(CuIn)_xS_2$, which were derived from measurements at the Cu edge for all samples. Obviously, the first peak at $R \approx 2.3 \text{ \AA}$, which corresponds the Cu-S distance, remains at the same position over the whole range of x . The higher shells about $R = 3.5 \text{ \AA}$ and 4.5 \AA show the expected change from the pure $CuInS_2$ to the ZnS phase. For $x = 1.0$ the FT could be fitted with the model of $CuInS_2$. Between $x = 0.69$ and $x = 1.0$ the higher shells of solid solution changes dramatically, probably due to the cubic to tetragonal phase transition. With decreasing x the surrounding of the second neighbour shell comes close to the ZnS phase, but the Debye-Waller factor is enlarged.

Fig. 2 displays the FT of the $Zn_{2-2x}(CuIn)_xS_2$ with $x = 0.57$ measured at the Cu, Zn and In absorption edges. The different nearest neighbour distances are clearly seen. The next nearest neighbour distances R_1 between the metal (Cu, Zn, In) and sulfur (S) as a function of the parameter x are shown in Fig. 3. Calculating an average metal - S distance from XRD data, depicted by the dotted line, one would also expect increasing atomic distances. But our experiment shows: (a) the three sulfur nearest neighbour distances do not vary significantly with x . (b) The structural phase transition from zinc-blende to chalcopyrite of $CuInS_2$ obviously does not influence the next nearest neighbour bond length.

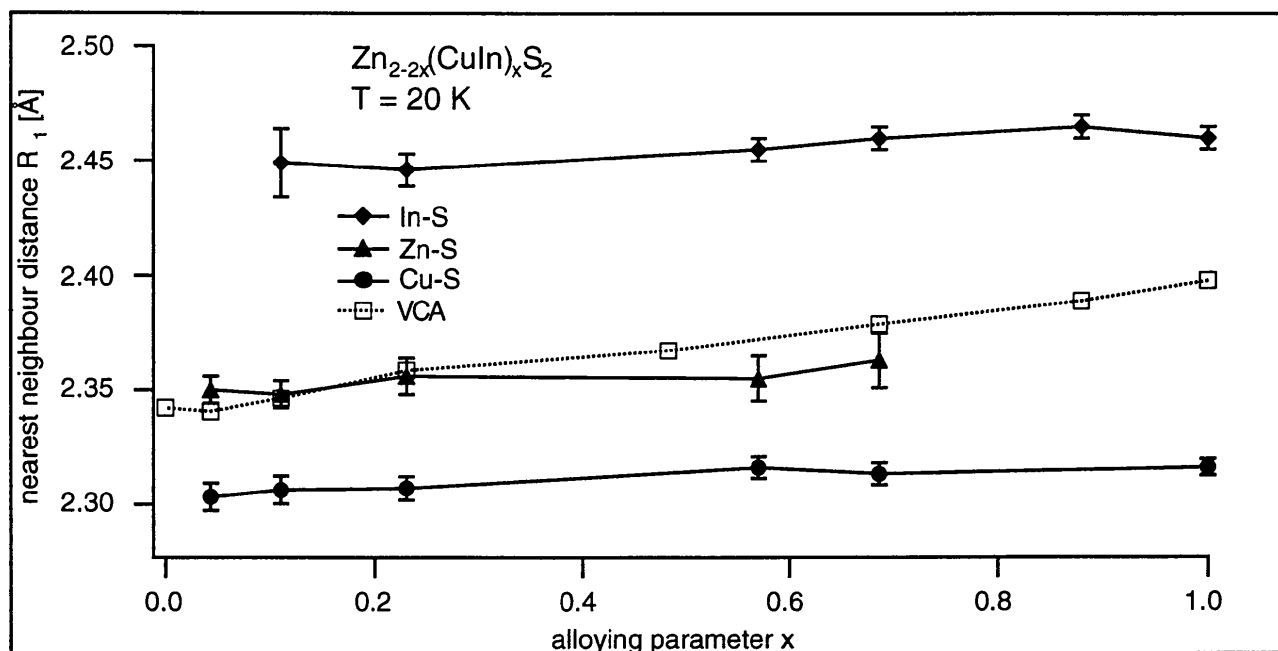


Figure 3

The atomic nearest neighbour distances obtained from fit results as a function of alloying parameter x measured at the Cu, Zn and In K-edge, respectively. Dotted curve is the average cation anion bond length (VCA) calculated from the measured x-ray lattice constant.

The next nearest neighbour shells were also analysed. Because of interference of different single and multi scattering paths and the different possible atoms (Cu, Zn, In) at about $R_2 \approx 3.91 \text{ \AA}$ and the next metal - S bond at $R_3 \approx 4.54 \text{ \AA}$ the determined atomic distances do not have meaningful result due to large error range. Nevertheless, the determined next nearest neighbour distances (R_2 , R_3) increase with the changes in x and the distances (R_2 , R_3) derived from XRD were found within their error range.

In conclusion, we found a fixed bond length for nearest neighbour (metal - S). Taking the composition change in account, this is in accordance with the increase of the lattice parameters.

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